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PROBLEMS OF QUALITY

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EFFECT OF THE COMPOSITION OF THE RESIDUAL ATMOSPHERE ON THE QUALITY OF ALUMINUM MIRROR SPRAYING

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The reasons for the emergence of spots that appear in large-sized mirrors are investigated. Practical recommendations for elimination of these spots are given.

Mirrors play an important role in interior decoration. A widely used method in mirror production involves deposition of aluminum by spraying in vacuum on a silicate glass surface. To obtain a smooth surface, glass melt is poured into a mold partly filled with tin. One of the varieties of defect is the appearance of spots whose color differs from the color of the mirror. Such spots appear on large-sized mirrors some time after spraying.

The purpose of the present study was to clarify the causes of the appearance of spots. With this aim, methods of direct analysis of the surface layers, namely, x-ray electron spectroscopy and secondary-ion mass spectrometry, were used.

The x-ray electron studies were performed on an upgraded ÉS-2401 spectrometer [1]. The spectra were excited by MgK_α radiation. The level of vacuum in the spectrometer chamber was 10^{-6} Pa. Concentration profiles over depth were obtained by bombardment with argon ions of energy 900 eV. The rate of glass etching was 0.4 nm/min, and that of metal coating etching was about 1 nm/min. To analyze deep-lying aluminum coating layers, etching in a KOH solution was carried out. The mass spectrometry of mirrors was performed on an MS-7201M mass spectrometer by bombardment with argon ions of 4 keV energy. The use of methods that to a certain extent duplicate each other is occasioned by the significantly higher degree of localization of the method of secondary-ion mass spectrometry, as compared to x-ray electron spectroscopy and its higher sensitivity to light elements. Aluminum coatings 7 – 8 μm thick produced by magnetron sputtering on silicate glass were investigated.

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The composition of the initial-glass surface and the compositions of mirrors after layer etching are given in Table 1, while Table 2 shows proportions of carbon, oxygen, and aluminum in the surface layer of defective mirrors and a pure mirror (layer by layer).

The initial composition is calcium silicate glass with La_2O_3 additive (to increase the surface tension). The glass structure can be represented as chains of silicon-oxygen tetrahedra joined to each other. As a result, a kind of lattice is formed. Calcium acts as a modifier, does not participate in the lattice construction, and is not incorporated in it. Ca^{2+} ions are linked to the surrounding oxygen atoms by less oriented bonds [2]. Ca – O bonds are weaker than Si – O bonds, and therefore any external action primarily affects calcium ions.

Surface cleansing by argon plasma in the sputtering-installation chamber can cause modifications in the composition of the glass surface before aluminum spraying.

The argon ions incorporated into the glass become neutralized by taking an electron from a nonbridge oxygen:

$$Si – O^- – M^+ + Ar^+ \to SiO^0M^+ + Ar^0.$$

As a result of the reaction, the bond of these ions with oxygen becomes weaker, and they can migrate freely in the sample under the action of electric fields developed by volume charges. The region of this action is limited to several tens of angstroms (near the surface), and the results become perceptible after 30 – 60 min of argon ion bombardment. A similar effect is observed under ion bombardment of lead silicate glasses: the amount of lead reduced in this way constituted up to 10% of its total content [3].

TABLE 1

Sample	Content, %											
	C	O	N	Al	Ca	F	Cl	Sn	S	Si	La	Na
Uncoated glass: argon, 5 min	10.80	59.50	0.25	–	4.28	–	–	0.17	–	22.20	2.30	0.40
Defective glass surface:												
argon, 20 min	33.00	39.80	0.84	24.80	0.34	0.70	0.25	0.05	0.20	–	–	–
1 min in KOH	61.80	23.90	1.07	12.80	0.78	0.23	0.20	0.03	0.10	–	–	–
2.5 min in KOH	73.70	16.70	1.80	5.70	1.60	0.30	0.10	0.05	0.10	–	–	–
7 min in KOH	76.40	16.20	1.50	0.80	1.90	0.30	0.20	–	0.23	2.36	–	–
Pure mirror:												
argon, 5 min	33.50	39.70	0.70	24.00	0.50	0.30	0.50	–	0.70	–	–	–
2.5 min in KOH	32.50	41.00	1.10	23.70	0.70	0.10	0.40	0.10	0.30	1.90	–	–
Pure mirror*	–	–	–	94.80	2.80	0.40	1.60	0.40	–	–	–	–
Spot site*	–	–	–	73.50	20.60	3.80	1.20	0.64	–	–	–	–

* The proportions of the main components, not taking into account carbon and oxygen, after etching of the surface layer in KOH for 2.5 min.

Oxygen can exist in glass in three forms: O^{2-}, O^-, and O^0. The amount of the first type of ions in high-silicate glasses is not large, and therefore, this form does not have a significant effect. O^0 covalently bonded with silicon has low activity. The ion O^- can participate in the following reactions:

$$SO_2 + \frac{1}{2}O_2 + 2O^- = SO_4^{2-} + O^0;$$

$$CO_2 + 2O^- = CO_3^{2-} + O^0;$$

$$H_2O + 2O^- + O^0 = 2(-O-H-...O-)^-.$$

These processes can accompany the process of ion cleansing of the glass surface.

According to the mass spectrometry data, the sites of spots contain more carbon, hydrocarbons, and calcium than the pure mirror sites.

It is known that the residual atmosphere that remains in the vacuum chamber after vacuum pumping employing available pumps contains hydrogen, water, carbon oxide (II), and various hydrocarbons with a chain length of 3 to 8 carbon atoms.

Water has a mineralizing effect, i.e., it facilitates formation of crystalline particles. The flat ions CO_3^{2-} have a similar effect.

The areas of spots exhibit a high content of carbon, hydrocarbons, and calcium. The sources of hydrocarbons can be forevacuum pipes (primarily during ion purification), diffusion pumps (in the course of spraying), and structural elements made of polymer materials. An additional factor affecting a freshly formed mirror is rapid inlet of the atmosphere after the end of spraying, since sputtering devices traditionally use electromagnet valves, which do not allow for gradual inlet of gases.

During abrupt inlet of the atmosphere, CO_2 and H_2O molecules from the air and, possibly, hydrocarbons from oils that are virtually always present on industrial premises are incorporated into the surface layer of the mirrors nearest to the valve. This is accompanied by corresponding reactions with glass components and diffusion of calcium toward the outer surface. The latter is caused by heating of the surface, which inevitably accompanies the spraying process.

TABLE 2

Sample	Content, %		
	C	O	Al
Defective mirror, initial surface	77.5	13.2	9.5
Defective mirror after argon treatment for:			
3 min	77.4	13.9	8.7
14 min	77.5	13.7	8.8
24 min	73.1	15.8	10.9
45 min	71.7	17.7	10.6
Pure mirror, initial surface	77.3	15.8	6.9
Pure mirror after argon treatment for:			
3 min	69.7	18.6	11.7
14 min	61.2	24.4	14.4
35 min	46.8	33.2	18.5
45 min	47.6	32.2	18.5

According to the method of predicting thermally stimulated modifications of the surface composition based on analysis of phase diagrams, the composition changes in the direction of the nearest minima on the liquidus curve. According to the phase diagram of $CaO - SiO_2$, the surface of silicate glasses of the composition considered [4] should exhibit enrichment in calcium. As a result, the sputtered surface layer of the mirror in areas where air molecules become incorporated is enriched in carbon and calcium. In deposition of aluminum on the surface, it is possible to produce a layer consisting of metallic aluminum and Al_2O_3. Depending on the composition of the residual atmosphere in the vacuum chamber, compounds that are thermodynamically more stable than Al_2O_3 can be formed, for instance: $Al_2O_3 \cdot 3H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, $Al_2O_3 \cdot CaO \cdot 2SiO_2$, $Al_2O_3 \cdot CaO$ [5].

The outward appearance (color) of these compounds differs from a pure film of aluminum deposited by spraying.

In studying defective mirror areas using a Neofot optical microscope (× 250), spherical microheterogeneities can be observed. It is known that in the initial stages deposition of a coating occurs in spots, and the larger the surface, the technically more difficult it is to obtain a continuous coating. In this case, the reason for the emergence of inhomogeneities is evidently tin residues on the glass surface (Table 1). These residues are visually imperceptible on the initial surface, which becomes highly activated as a result of ion-plasma treatment. Two processes are possible after that. First, tin is a classical opacifier and imparts opacity to glasses due to local microcrystallization. Second, tin can react with air components. Both these processes are slow under normal conditions but can be catalyzed under ion-plasma treatment.

Based on the results obtained, the following recommendations can be given:

– surface preparation for spraying should include thorough removal of tin residues; a device for effective chemical polishing is described in [6];

– it is necessary to use traps that prevent penetration of oil vapors from the pumps into the spraying chamber;

– it is desirable to monitor the composition of the residual atmosphere in the chamber with at least a simple mass-spectroscopy sensor;

– passivation of the surface directly after spraying can be performed by letting in a dried inert gas or nitrogen;

– the chamber design should provide for scatterers that prevent “impact” of air against the freshly sprayed surface.

REFERENCES

1. O. M. Kanunnikova, F. Z. Gil’mutdinov, V. I. Kozhevnikov, and V. A. Trapeznikov, *Methods of Photoelectron Studies of Inorganic Materials* [in Russian], Izhevsk (1992).
2. A. A. Appen, *Chemistry of Glass* [Russian translation], Khimiya, Leningrad (1970).
3. M. F. Sorokina, O. M. Kanunnikova, F. Z. Gil’mutdinov, and V. I. Kozhevnikov, “A study of binary lead-silicate glasses using the x-ray electron spectroscopy method,” *Steklo Keram.*, Nos. 1 – 2, 12 – 14 (1996).
4. M. A. Toropov, V. P. Barzakov, V. V. Lapin, and N. N. Kurtseva, *Phase Diagrams of Silicate Systems, Reference Book, Issue 1* [in Russian], Nauka, Leningrad (1969).
5. M. Kh. Karapet’yants and M. L. Karapet’yants, *Main Thermodynamic Constants of Inorganic and Organic Substances* [in Russian], Khimiya, Moscow (1968).
6. V. A. Perevoshchikov and V. D. Skupov, “Devices for chemical etching and polishing of plate surfaces,” *Zavod. Lab.*, No. 4, 37 – 44 (1997).